

4853**M.Sc. (CBS) Ist Semester Examination****CHEMISTRY****[Physical Chemistry (Theory-I)]****(DSC)****Paper : CHEM-103****Time : Three Hours]****[Maximum Marks: 80**

Note : Question paper comprises ten questions. The candidates are required to attempt *five* questions, selecting *one* question from each unit. All questions carry equal marks.

UNIT-I

1. (a) Explain different signals and their splitting that will be observed in NMR spectrum of Crotonaldehyde. (8)
- (b) Briefly discuss different factors affecting chemical shift and spin-spin coupling in NMR spectrum. (8)
2. (a) Briefly explain Zero field splitting in ESR spectroscopy. (8)
- (b) A Mossbauer nucleus has spin $5/2$ and $3/2$ in its excited and ground states, respectively. How many lines will the γ -ray spectrum split if (i) Nucleus is under the influence of an internal electric field gradient but no magnetic field, (ii) there is no electric field gradient at the nucleus but an external magnetic field is applied? (8)

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UNIT-II

3. (a) Briefly explain rotational energy level and spectrum of Non-rigid diatomic rotator. (8)
- (b) Calculate the rotational constant and hence moment of inertia and bond length of HF^{19} molecule which shows a series of equidistant lines 0.8413 cm^{-1} . (8)
4. (a) Briefly explain why intensity of rotational spectrum lines first increases and then decreases. (8)
- (b) Briefly explain the following :
- (i) Rule of mutual exclusion.
- (ii) Change in shape, size or direction of polarizability ellipsoid of water molecule during three vibrational modes. (8)

UNIT-III

5. (a) Briefly explain kinetics of $\text{H}_2\text{-Br}_2$ thermally induced chain reaction. (8)
- (b) Briefly explain Rice Herzfeld mechanism of decomposition of acetaldehyde molecule. (8)
6. Write a short note on the following :
- (i) Competitive reactions.
- (ii) Principle of microscopic reversibility.
- (iii) Relation between reaction rate and chemical equilibrium if any.
- (iv) Consecutive reactions. (4,4,4,4)

UNIT-IV

7. (a) Briefly explain transition state theory to find reaction rate. Also write down advantage of TST over collision theory. (8)
- (b) Discuss in detail Hinshelwood treatment of Unimolecular reaction. (8)
8. (a) Write a short note on the following :
- (i) Diffusion controlled reactions.
- (ii) Importance of potential energy surface in Thermodynamics. (8)
- (b) Write down the limitations of Lindemann theory of unimolecular reactions and how they are removed by Hinshelwood treatment? (8)

UNIT-V

9. (i) Differentiate between Hinshelwood and Eley-Rideal mechanism of adsorption.
- (ii) Briefly explain Langmuir mechanism of adsorption. (8,8)
10. Briefly explain the Flash photolysis and Stop flow methods to find rate of fast reactions. (8,8)
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